Monsanto

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December 13, 1993

Ms. Pat Reitz
U.S. Environmental Protection Agency
Region 7
WSTM Division/RCRA Branch
726 Minnesota Avenue
Kansas City, Kansas 66101

Re: Monsanto - J. F. Queeny Plant
RFI Phase II Soil Sampling

Dear Pat:

This letter is to follow up on two items you and I discussed on the phone several weeks ago regarding soil sampling for the Phase II RFI.

1. I talked to Monsanto's Environmental Sciences Center (ESC) about the field test kits for PCB analysis. They proposed that instead of using the field kits we send the samples to them. They committed to give us 24-hour turn-around on the samples using a GC method in the lab. After some discussion, we have decided to use this method, if the Agency approves. Two copies of a Standard Operating Procedure (SOP) developed by the ESC are enclosed for your review. We would still use this method for "screening" and plan to send confirmatory samples to Savannah Labs when we think we have delineated the extent of the PCBs.

2. At our September 17, 1993 meeting at the Queeny plant, when we discussed the analytical parameters for the soil samples to be collected in the former quarry area (Section 3.2 of the workplan), the Agency requested that we run VOCs and alachlor in addition to BNAs and metals. It was our understanding that we had agreed to run the VOCs and alachlor on one of the samples collected at each location, not each sample as stated in the Agency's October 14, 1993 letter. When you and I talked about this, you agreed to reconsider this request.

We have not yet received final results from Savannah Labs on the groundwater samples collected last month. Once we receive those results and a response from you on these issues, we will schedule the soil sampling.

I hope you are feeling well and enjoy the holidays. If you have any questions, please call me at 314-694-6127. I'll be in the office until the 22nd and then out until the 4th of January.

Sincerely,

Jo Hanson

Jo S. Hanson
Project Manager

Procedure for Rapid Extraction and Analyses of Aroclor Formulations (A1232, A1016, A1242, A1248, A1254, A1260 and A1262) Using Ultrasonically Aided Extraction of Solids

1. Scope and Application:

1.1. This Standard Operating Procedure is an adaptation of SW-846 Method 3550. This method is also an adaptation of Monsanto's Environmental Sciences Center Standard Extraction Methods WSEX02 and PCEX02. This document describes a procedure for the extraction of PCBs (Aroclor formulations) from solids such as soils, sludge, and wastes using ultrasonic agitation to ensure intimate contact of the sample matrix with the extraction solvent.

1.2. This method is applicable only to the isolation, concentration, and analyses of PCBs from solids that are expected to contain concentrations of PCB formulations that are >0.1 mg/kg. It is not applicable to samples that are expected to contain relatively low concentrations of PCBs (<0.1 mg/kg). Therefore, sections of SW-846 Method 3550 that are pertinent only to low organic concentration samples will not be addressed in this document.

1.2.1. This method is applicable only to the preparation of samples for screening and analyses of PCB formulations using a capillary gas chromatograph equipped with an electron capture detector. It is only applicable to the preparation of samples for the analysis of Aroclor formulations. This method does not apply to the preparation of samples for the analyses of Aroclor 1221. Quantitiative results of this method may be less accurate if mixtures of formulations are present.

1.3 Specific samples may require additional cleanup steps. See SW-846 for applicable methods.

2. Summary of Method:

2.1 *Low concentration method*: Not applicable.

2.2 *High concentration method*: A weighed sample amount is dried by the addition of sodium sulfate and ultrasonically extracted with methylene chloride. The extract is dried and, as necessary, exchanged into a solvent compatible with the instrumental procedure to be used.

3. Definitions

3.1 Internal standard -- A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate analyte -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. The purpose of a surrogate analyte is to monitor extraction performance with each sample.

3.3 Laboratory duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.5 Laboratory reagent blank (LRB) -- An aliquot of clean soil that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field reagent blank (FRB) -- Clean soil placed in a sample container while in the field and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Laboratory performance check solution (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory fortified blank (LFB) -- An aliquot of clean soil to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.9 Laboratory fortified sample matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and it's purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock standard solution -- A concentrated solution containing compounds that are method analyte(s). Stock standard solutions are used to prepare primary dilution standards.

3.11 Primary dilution standard solution -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality control sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

3. Interferences:

3.1 Interferences are specific to individual analytes. See Method 3500 for more information.

4. Equipment and Reagents:

4.1 Spatula (stainless steel or Teflon) or other device for mixing and weighing sample.

4.2 *Ultrasonic cell disrupter*: Heat Systems -- Ultrasonics, Inc., Model W-385 (475 watt) sonicator (or equivalent - must be a minimum of 375 watts with pulsing capability) and Ho. 200; 1/2" Tapped Disrupter Horn plus No. 207; 3/4" Tapped Disrupter Horn, and No. 419; 1/8" Standard Tapered micro tip probe.

4.3 *Sonabox*: Recommended with above disrupters for decreasing cavitation sound: Heat Systems -- Ultrasonics, Inc., Model 4328 (or equivalent).

4.4 *Disposable Pasteur pipettes*: Flint or borosilicate glass.

4.5 *Beakers*: Various sizes as needed.

4.6 *Balance*: Top-loading, capable of accurately weighing 0.01 g.

4.2 *Vials*: Glass 2, 10, 20 and 40 -mL capacity, borosilicate glass with Teflon-lined screw caps

4.7 *Graduated cylinders*: Various sizes as needed.

4.8 *Adjustable volume micro pipettors*: Gilson adjustable volume pipettes P-200 and P-1000 adjustable volume pipettes (or equivalent).

4.9 Hewlett-Packard 5890 GC (or equivalent) equipped with a splitless injection port, and electron capture detector.

4.10 J&W - DB-5 (30 meter x 320 micron I.D. capillary column).

4.11 Hewlett-Packard 7673 autosampler or equivalent.

4.12 Dionex AI-450 chromatography software version 3.2 or later.

4.13 Miscellaneous gas chromatograph supplies such as septa, injection port liners etc.

4.14 Lotus 123 for windows software or equivalent.

4.15 IBM compatible 286, 386,486 or greater PC with 40 mB hard drive or equivalent.

5. Reagents:

5.1 *Sodium Sulfate*: (ACS) Granular, anhydrous, purified by heating at 400°C for 4 hr in a shallow tray. Baker #7398 (or equivalent).

5.2 *Extraction solvent*: Methylene chloride (pesticide quality or equivalent).

5.3 *Reagent water*: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest. Suitability of water shall be determined by the analyst. De-ionized water or Burdick and Jackson Distilled in glass water may be suitable.

5.4 *Sulfuric Acid Solution (1:1)*: Slowly and in small increments add 50 mL of concentrated H_2SO_4 to cold reagent water.

5.5 *Standard Solutions:* Internal standard solution, surrogate standard solutions and Aroclor formulation standard solutions.

5.5.1 PENTACHLORONITROBENZENE (PCNB) 98% purity, for use as internal standard, or surrogate standard

5.5.2 2,4,6-TRICHLOROBIPHENYL (TCB) 96% purity, for use as surrogate standard (available from Chemicals Procurement Inc.).

5.5.3 PENTACHLOROBENZENE (PCLB) 98% purity for use as a surrogate standard.

5.5.4 HEXACHLOROBENZENE (HCB) 98% purity for use as an internal standard.

5.5.5 DECACHLOROBIPHENYL (98%) purity for use as a surrogate standard

5.5.6 OCTACHLORONAPHTHALENE (98%) for use as an internal standard

5.5.7 DECAFLUOROBIPHENYL (98%) for use as a surrogate standard.

6. Sample Collection, Preservation and Handling:

6.1 Samples shall be collected in containers appropriate for the analysis (to be determined by the study director).

6.2 Samples shall be shipped cold (refrigerated).

6.3 Samples shall be refrigerated until completion of analyses.

6.4 Samples shall be analyzed within 24 hours of receipt.

6.5 Samples shall be handled utilizing proper safety precautions (wearing of gloves, in hood, etc.).

7. Procedure (Extraction and Preparation)

7.1 *Physical preparation of samples*: before extraction.

7.1.1 *Sediment/soil samples*: Decant any water layer on a sediment sample and discard. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 *Waste samples*: Samples consisting of multiple phases must be prepared by the phase separation method in SW-846 before extraction. This procedure is for solids only.

7.2 *Determination of percent moisture*: Sample concentrations will be reported on a weight basis as received, without moisture determination during rapid sample analyses. Samples should be relatively dry for this analysis.

7.3 *Extraction method for samples expected to contain high concentrations of organics (>0.1 mg/kg)*:

7.3.1 After the samples have been physically processed (see Section 7.1), weigh an aliquot of approximately 2 g (record weight to the nearest 0.01 g) of sample into a 20-mL vial. The aliquot shall be made representative of the original sample to the extent judged feasible by the analyst. Any noticeable differences between the original sample and the aliquot shall be recorded in a laboratory notebook or on the sample work up sheet. Wipe the mouth of the vial with a tissue to remove any sample material before recording the exact weight of the aliquot. Cap the vial before proceeding with the next sample to minimize cross contamination and the loss of any volatile components.

7.3.2 Add approximately 2 g of anhydrous sodium sulfate to each aliquot and mix well. Additional sodium sulfate may be added until the analyst judges the sample to be adequately dried.

7.3.3 Spike the sample with a Surrogate Spiking standard and prepare a simulated surrogate spike representing 100% surrogate recovery.

7.3.4 Immediately add whatever volume of methylene chloride is necessary to bring the final extract volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8-in. tapered micro-tip ultrasonic probe for 2 min. at output control setting 4 and with mode switch on pulse and percent duty cycle at 60%.

7.3.5 Extracts containing substantial amounts of suspended solids should be clarified by centrifugation or by filtration through disposable Pasteur pipettes loosely packed with 2- to 3-cm Pyrex glass-wool plugs or membrane filters. Extracts which are to be retained for any length of time should be filtered to prevent reabsorption of the extractables onto the sample matrix. Retained extracts which have not been filtered prior to storage should be disrupted according to Section 7.5.4 prior to removal of an aliquot for analysis.

7.3.6 The extract is now ready for cleanup or analysis, depending on the extent of interfering compounds.

7.3.7 Remove approximately 2 mL of the extract and add it to a 10 mL vial. Add approximately 2 mL sulfuric acid solution, and shake for approximately 30 seconds. Allow the phases to separate

7.3.8 Remove 200 uL of the extract and combine with 200 uL internal standard solution in an autosampler vial.

8. Calibration and Calculations

8.1 Aroclor Formulation Calibration

8.1.1 When formulations of individual compounds are being analyzed (i. e. Aroclors or Toxaphene) it is more reliable to base the analysis of the formulation on a number of individual compounds. This is done by creating an analysis method for each of the formulations in which the analyst is interested. Usually more than 10 compounds are assigned arbitrary names (i. e. "Aroclor 1254 Peak #1", "Aroclor 1254 Peak #2", "Aroclor 1254 Peak #3", etc.). If the Aroclor concentration is used for the concentration of each of these 10 or more compounds, then the analysis of an unknown compound would result in 10 or more determinations for the Aroclor concentration. The 10 values can then be averaged and statistics such as % Relative Standard Deviation (%RSD), etc. can be calculated. This increased information can be used to statistically evaluate the validity of the Aroclor formulation identity and its concentration. Figure 1 summarizes this approach.

8.1.2 In order to determine which formulation is present in an extract, visual comparison can often be used. However, a more rigorous comparison involves creating an analytical method for each Aroclor formulation. When the method is calibrated with the corresponding formulation and the unknown formulation is reanalyzed using this calibrated method, the method resulting in the lowest %RSD will define which formulation is present. Furthermore, the average of all of the peaks in that method will give the Aroclor concentration.

8.1.3 An alternate method of calculation may be used to calculate the concentrations of PCBs, or any other multicomponent mixture where compounds are not available singly and the formulation is well defined. This method involves preparing a standard from the formulation at a known formulation concentration (i.e. Aroclor 1254 at 1 μg/mL)

8.1.4 One mode of iterative determinations requires that an average concentration (X_{av}) is determined from a number of congeners which are detected (N) using response factors generated using ether internal or external standards. The average concentration is doubled $\{2*(X_{av})\}$ and halved $\{1/2(X_{av})\}$, and all peaks outside these low and high criteria (C_1 and C_2) are eliminated from the next calculation of the average (X_{av1}). Once again, the average is doubled $\{2*(X_{av1})\}$ and halved $\{1/2*(X_{av1})\}$and peaks (N_1) outside these low and high criteria are eliminated in the next calculation of the average (X_{av2}). This procedure is repeated until all peaks are within the calculated criteria ($N_i=N_{i+1}$). After these conditions are met the average concentration is reported as the formulation concentration.

8.1.5 Another method of formulation concentration determination is exactly the same as those described in 8.1.4 except the median is used to set the low and high criteria for average concentration determination. This method is not iterative.

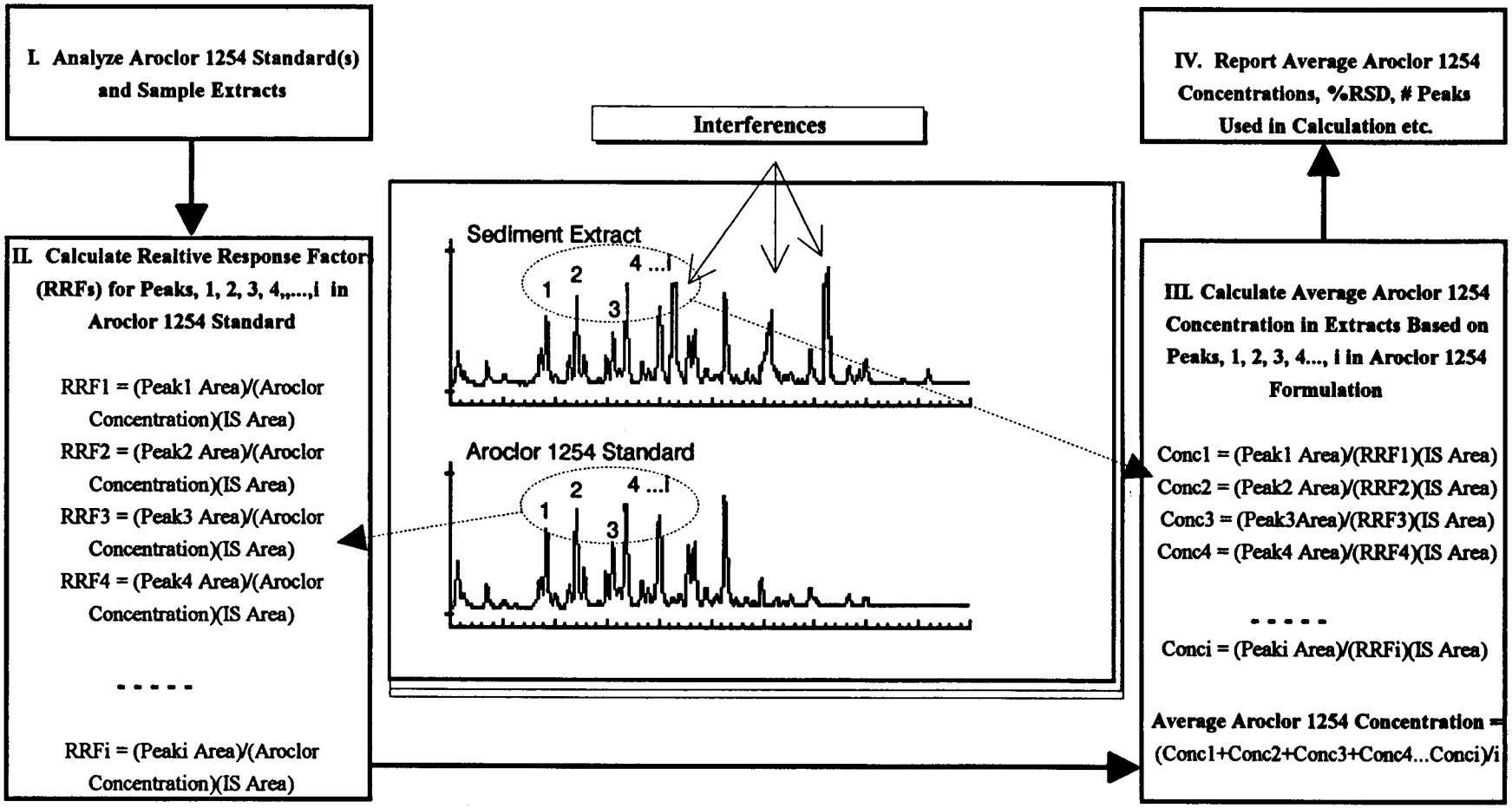

Figure 1. Summary of PCB Quantitation Approach for Aroclor 1254

8.2. Calculations

8.2.1 Calculate analyte concentrations in the sample from the response for the analyte using the calibration procedure described in Sect. 8.1.

8.2.2 Analyze each calibration standard according to the procedure (Sect. 8.1). Tabulate response (peak area or peak height) against the concentration for each compound and internal standard. Calculate the relative response factor (RRF) for each analyte and surrogate using Equation 1. This equation uses the internal standard calibration procedure. Calculate the concentration (C) in the sample using the calibration curves and relative response factors (RRFi) determined in Sect. 8.1 for each named congener by Equation 1.

$$RRF_i = \frac{(A_i)(C_{is})}{(A_{is})(C_f)} \qquad \text{(Equation 1)}$$

where :

A_i = Response of the ith congener in the formulation.
A_{is} = Response of the internal standard.
C_{is} = Concentration of the internal standard (μg/mL).
C_f = Concentration of the formulation to be measured (μg/mL).

8.2.3 The concentration (C) in the sample can be calculated from Equation 2.

$$C_f\,(\mu g/g) = \frac{(A)(V_t)}{(W_s)} \qquad \text{(Equation 2)}$$

where:
A = Average formulation concentration in the extract (μg/mL).
V_t = Volume of total extract (mL).
W_s = Weight of soil extracted (g).

$$A = (C_{f1} + C_{f2} + C_{f3} + ...C_{fi}) / i \qquad \text{(Equation 3)}$$

8.2.4 These calculations are still used when using the average or median based criteria described in section 8.1, although the result is based on more than one determination.

9. Gas Chromatographic Conditions

9.1 Analyses are conducted on a Hewlett-Packard Gas chromatograph equipped with a capillary column and an electron capture detector, or equivalent.

9.2 Column: J&W-DB-5: 30 meter x 320 micron I.D capillary column or equivalent. (Note: other capillary columns with different stationary phases may be used, providing adequate resolution of the PCBs congeners can be demonstrated to allow for Aroclor formulation identification.)

9.3 Gas chromatographic conditions: Injection port temperature: 240 °C , Injection mode: splitless, Detector temperature 302 °C, and Column head pressure: 5-8 P.S.I..

9.4 GC - oven temperature program: Initial temperature: 150 °C for 2 minutes ramped at 9 °C/minute until a final temperature of 300 °C is reached. Final temperature hold times may vary from 5 to 10 minutes.

10. Analyses

10.1 Samples and standards are prepared for analyses as described in section 7.3.8.

10.2 Once the formulation is identified in the sample matrix, a series of authentic Aroclor formulation calibration standards should be analyzed along with the samples. Recommended concentrations are 0.1, 1, 5, and 10 ppm. The 1, 5, and 10 ppm standards should be used to generate the calibration curves for each chosen congener. The 0.1 ppm standard should be analyzed with each series of samples to assure the accuracy of reported results at low concentrations.

10.3 After preparing the samples and standards, the vials should be placed in the autosampler tray and injected.

10.4 Data should be re analyzed with the Dionex laboratory data system to create a Lotus 123 delimited file, which should be imported into a template file which the Environmental Sciences Center has developed to perform the average and median based calculations which are described in section:8.1.

10.5 Results should be forwarded to analyses requester.

11. Quality Control:

11.1 A quantity of reagent blanks and matrix spike samples shall be prepared equal to or greater than 10 % of the total number of sample extracts.

11.2 All reagent blanks and matrix spike samples shall be subjected to exactly the same analytical procedures as those used on actual samples.

12. References:

12.1 US EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

12.2 US EPA, "Inter laboratory Comparison Study: Methods for Volatile and Semi-volatile Compounds," Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.

12.3 US EPA, "Test Methods for Evaluating Solid Waste; Physical/Chemical Methods," Volume 1 Section B, Third Edition, Office of Solid Waste Publications.

12.4 "Examples of the Use of An Advanced Mass Spectrometric Data Processing Environment For The Determination of Sources of Waste," presented at the Fifth Annual Waste Testing and Quality Assurance Symposium, By B.M. Hughes, D.E. McKenzie, C.K. Trang, and L.R. Minor, 1989.